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14. ABSTRACT

In summary, CdTe nanocluster, CdTe QD with different emissions can be synthesized by carefully controlling the synthetic parameters. We observed that the non-emitting nanocluster exhibits distinguishable extinction at 446 nm. The two photon studies reveal that the two photon absorption of cluster sample is slightly higher than the QD samples. We speculate that most of the absorbed energy was transferred to phonon vibration and localized heat which may be used in wide range of applications. In order to fully understand the energy dissipation/conservation in cluster, ongoing studies such as the 2PA cross-section as a function of excitation wavelength can be proposed.

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Final Performance Report

Preparation and Two-photon Characterization of Ultrasmall CdTe Quantum Dots

1. Synthesis of CdTe nanocluster (diameter ~2.2 nm) and nanodot (diameter 3.2 ~ 4.6 nm) in aqueous media

Firstly, tellurium powder and sodium borohydride were mixed with nitrogen-saturated water. The mixture was stirred for 0.5–1 hour until it became light-pink color. This solution is herein referred as the Te precursor. Next, cadmium chloride, mercaptopropionic acid, and nitrogen-saturated water were loaded into a 100 ml three-necked flask under stirring. The pH was adjusted to 8 by adding dropwise sodium hydroxide solution. The flask was sealed and subsequently the Te precursor was injected into the mixture under nitrogen atmosphere. Without heating the mixture, the aliquots were withdrawn and the nanoclusters were separated from the surfactant solution by the addition of ethanol and centrifugation. For nanodots synthesis, the mixture was refluxed at 100ºC. Different emission spectra (515 to 700nm) were obtained by varying the refluxing time. At the desire emission wavelength, the nanodots were purified from the surfactant solution by the addition of ethanol and centrifugation.

The aqueous synthesized QDs were transferred to organic phase by exchanging the capping ligand from mercaptopropionic acid to dodecanethiol. Briefly, purified QDs were dispersed into water, then a mixture of dodecanethiol, butanol and acetone was added. After stirring for 2 minutes, ammonium hydroxide was added to activate the dodecanethiol. After 30 minutes, the transferred QDs were purified and re-dispersed in toluene by the addition of ethanol and centrifugation.

Figure 1 shows the absorption and emission spectra of as-prepared nanomaterials. It is clearly shown that the position of absorption/emission peak is size-dependent. Red shift of the absorption/emission peak was obtained when the particle size became larger. It is worth mentioning that no luminescence signal was detected from the cluster while an absorption peak at 446 nm was noticeable, suggesting that new optical behavior may be generated from the material with dimension close to an atomic scale (i.e. cluster).

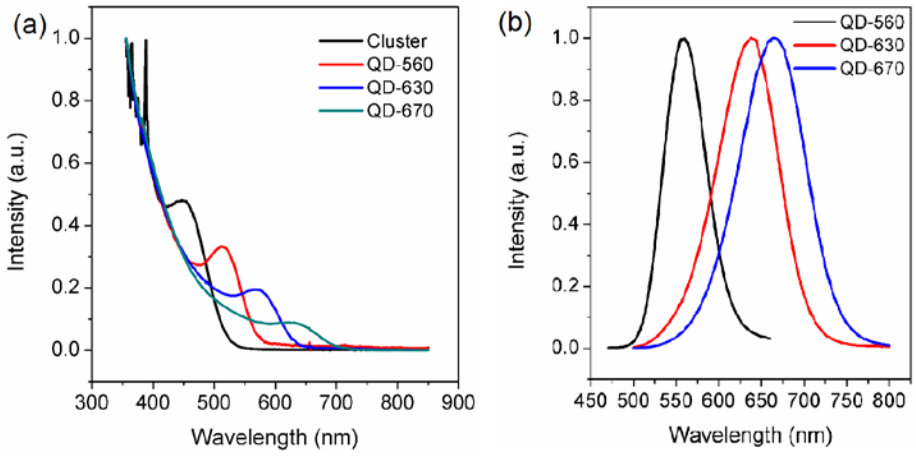

Fig. 1 (a) Absorption and (b) emission spectra of as-prepared cluster and QD.

The development of CdTe has received remarkable progress over the past two decade. The widespread application of CdTe QD, ranging from bioimaging to electronics, was owing to the unique optical and electrical properties [1-5]. Underlying the quantum confinement effect, CdTe QD exhibits size dependent emission. An extensive study of visible emitting CdTe QD can be easily found from the literature. Michalet et. al. reported the relationships between the emission peaks and the sizes of different QDs [6]. The curve represented CdTe is shown in Figure 2 (solid curve). Base on Figure 2, we estimate the size of QD-560, QD-630 and QD-670 as ~3.2 nm, ~4 nm and ~4.6 nm respectively. The size of cluster is ~2.2nm that is shown in the inset of Figure 2 is out of their study range (dotted curve, Figure 2). Nevertheless, the nonlinear optical phenomena, such as two-photon absorption, of these nanomaterials would be of great interest to the scientific community. In our recent report, two-photon absorption properties of ultrasmall CdTe nanocluster, CdTe QD and two photon dye (AF350) will be studied and compared.

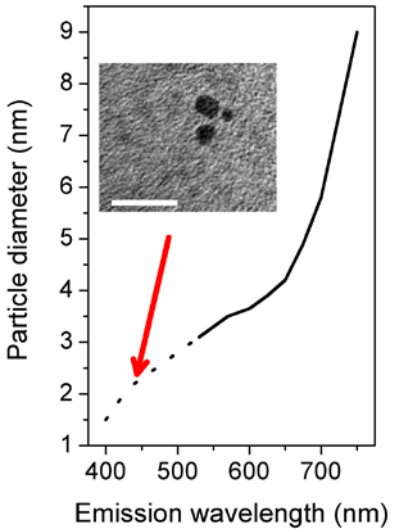

Fig. 2. Relationship of the emission peaks and the sizes of CdTe QDs [6]. Inset is the TEM picture of cluster (scale bar: 5nm)

2. Characterization of two-photon absorption (2PA) properties of samples

CdTe cluster and three CdTe QDs solutions in toluene have been measured by using nonlinear transmission method to determine their TPA cross-section values. The input laser wavelength, pulse duration and repetition rate were ~780 nm, ~160 fs and 1 kHz. The optical path-length of all tested samples was 1 cm, the laser beam was focused via an f=20-cm lenz on the center of the sample. AF350 dye solution in THF was employed as a comparison sample. According to 2PA theory, the nonlinear transmission of a two-photon absorbing sample can be expressed as

$$T(I_0) = \frac{Ln(1+\beta L I_0)}{\beta L I_0}$$

Here I_0 is the incident laser intensity, L is the path-length of the sample medium, β is 2PA coefficient of the sample material.

$$\beta = \sigma_2 N_0$$

Here σ_2 is the 2PA cross-section of an 2PA absorbing center, N_0 is the density of the center.

3. Final measurement results

The final results of 2PA cross-section values of the tested samples measured at ~780-nm wavelength and ~160-fs pulse regime are summarized in Table 1.

Table 1 Two-photon absorption (2PA) cross-section values of CdTe clusters and quantum dots solutions, measured by ~775-nm and ~160-fs laser pulses.

	Cluster	QD-560	QD-630	QD-670	AF350 (2PA dye)
Particles' size	~2.2 nm	~3.2 nm	~4 nm	~4.6 nm	
Solvent	toluene	toluene	toluene	toluene	THF
Weight concentration	20 mg/mL	20 mg/mL	20 mg/mL	20 mg/mL	13 mg/mL
Sample length	1 cm	1 cm	1 cm	1 cm	1 cm
Chemical unit (Molecular weight)	240	240	240	240	1306
2PA Cross-section (per chemical unit)	10.3 GM	8.1 GM	8.6 GM	9.4 GM	127 GM

Figure 3 shows the measured nonlinear transmission data as a function of the input laser pulse energy for the five tested sample solutions.

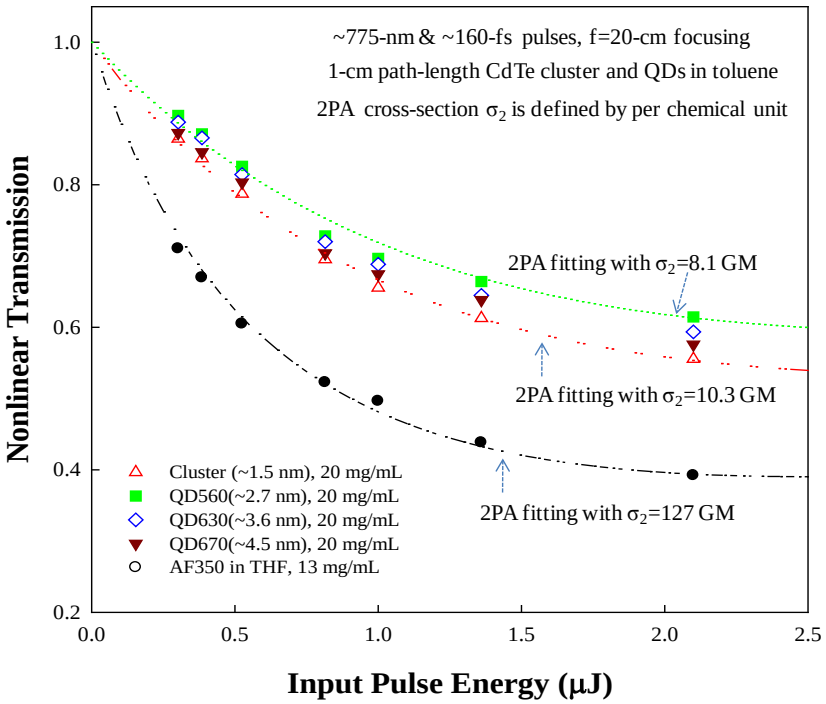

Fig. 3 2PA-induced Nonlinear Transmission of CdTe Cluster and QDs Solutions in Toluene

From Table 1 and Fig. 3, we can see that (1) there is no significant difference of the measured 2PA cross-section values between the CdTe cluster sample and three CdTe quantum dots samples; (2) the 2PA cross-section values (calculated per chemical unit) of CdTe samples are in an order of magnitude less than AF350/THF solution sample, measured at the same ~780-nm wavelength range; (3) the two-photon absorbing capabilities per unit weight of the solute are nearly in the same order of magnitude for the CdTe samples and AF350 organic dye sample.

In conclusion, CdTe nanocluster, CdTe QD with different emissions can be synthesized by carefully controlling the synthetic parameters. We observed that the non-emitting nanocluster exhibits distinguishable extinction at 446 nm. The two photon studies reveal that the two photon absorption of cluster sample is slightly higher than the QD samples. We speculate that most of the absorbed energy was transferred to phonon vibration and localized heat which may be used in wide range of applications. In order to fully understand the energy dissipation/conservation in cluster, ongoing studies such as the 2PA cross-section as a function of excitation wavelength can be proposed.

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